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INFLUENCE OF CARBON MONOXIDE ON THE RATE OF DEPLETION OF NO_X IN THE OZONATION OF THE HUMID EXHAUST GASES

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ABSTRACT

Reactions involved in the ozonation of NO_x present in exhaust gases are discussed. Associated reactions of Carbon monoxide, which is usually present in the exhaust gases, are also presented with particular reference to the case when moisture is present. A reaction scheme for the combined effect of ozonation of humid mixtures of CO and NO_x is presented. A reaction model for the scheme of combined ozonation of CO and NO_x is formulated. A discussion on the rates of reactions already published in the literature is presented. The model is analyzed based on the already published reaction rate equations. The rate of depletion of NOx in the overall ozonation reactions of NO_x in the exhaust gases with the respective depletion rates of associated carbon monoxide is presented.

Keywords

Exhaust, NOx, Ozone, Carbon Monoxide, Ozonation

1 INTRODUCTION

Industrial furnaces and internal combustion engines usually consume solid, liquid or gaseous fossil fuels of varying compositions of carbon, hydrogen, oxygen, nitrogen and sulphur. The combustion reactions within the furnaces and engines produce carbon dioxide, water vapour, carbon monoxide, oxides of nitrogen, traces of hydro carbons, elemental carbon in the form of soot in addition to the remaining nitrogen (Bond et al., 1972). It is reported that 236,000 tonnes of nitrous oxides (NOx) have been released to the atmosphere by combustion activities of fossil fuels in Malaysia in 1998. (Ministry of Science, Technology and Environment, Malaysia, 2000), (Ahmad Hj Mohd Sharkan, 2002). NOx usually consist of Nitrogen dioxide (NO_2) and nitric oxide (NO). The latter is not considered to be a harmful to health. However, NO reacts with other gases present both in the atmosphere, to form nitrogen dioxide. Nitrogen dioxide is harmful to health.

Generally, the environmental regulations impose limits on these emissions to tolerable values before release to the atmosphere. However, reduction of these emissions is usually carried with difficulty and at high expense.

Catalytic converters are usually employed in order to convert the carbon monoxide to carbon dioxide in the exhaust of IC engines. A catalytic converter working under ideal conditions would have an active use of about 100,000 km (Tharmarajah, 2000). The ideal working

temperature of catalytic converters is within the range of 400°C and 800°C. But due to possible temperature fluctuations below and above the above ideal ranges makes the converters less effective. Further, CO catalytic converters do not convert NOx. The SO_2 can be oxidized to SO3 and subsequently to sulphuric acid by the converter making the catalyst less efficient. Many studies have been carried out in the past to reduce NOx emissions of internal combustion engines. Techniques such as exhaust gas recycling and De-NO_x processes are reported in the literature. (Tharmarajah, 2000). The former technique which is recycling part of exhaust gases back to the engine inlet has proved success but with the expense of shaft power and increased levels of carbon monoxide emissions. Use of water emulsified fuel is reported to reduce the NOx emissions by 80-85% and particulate matter by 86-90%.Thermal De-NOx processes where NO is reduced to N_2 by means of catalysts and/or ammonia are also reported (Lyon, 2001).

Gases such as oxides of nitrogen are well known for their properties of ozone depletion in the stratosphere leading to much concern among the environmentalists. Overall reactions that occur in the stratosphere depleting the atmospheric ozone are presented in the literature (Emedia Science Ltd, 1998). The reactions of atmospheric ozone with NO_2 and the subsequent chain reactions are documented (Carpenter et al., 1998)

2. OZONE DEPLETION REACTIONS IN THE ATMOSPHERE

The typical ozone depletion reactions (Carpenter et al., 1998) of the atmosphere can be presented as follows.

A molecule of NO_2 reacts under the influence of light energy to form NO and a singlet [O] atom. The extent of the reaction depends on the intensity of the radiation of light.

$$NO_2 + h\nu \rightarrow NO + [O] \quad (1)$$

Ozone is degraded by energy from light radiation, producing a charged form of singlet oxygen, [O], and more molecular oxygen. This reaction is reported to proceed at a much slower rate than the first reaction.

$$O_3 + h\nu \rightarrow O_2 + [O] \quad (2)$$

Some of the charged oxygen atoms react with water molecules to form a hydroxyl radical, [OH] which are fragments of molecules that have at least one unpaired electron, and are highly reactive.

$$[O] + H_2O \rightarrow [OH] \quad (3)$$

The Hydroxyl radical [OH] reacts strongly with Carbon monoxide to form carbon dioxide and $[HO_2]$ radicals.

$$CO + [OH] \rightarrow {}^{O}{}_{2} \rightarrow CO_2 + [HO_2] \quad (4)$$

Other reactions with the Hydroxyl radical are

$$[OH] + O_3 \rightarrow [HO_2] + O_2 \quad (5)$$

The $[HO_2]$ radicals formed above react with the extra NO to form more NO_2 and more [OH] radicals.

$$[HO_2] + NO \rightarrow NO_2 + [OH] \quad (6)$$

$$[HO_2] + O_3 \rightarrow [OH] + 2O_2 \quad (7)$$

The hydroxyl radicals also react with NO and NO_2 to form acids HNO_2 and HNO_3 .

$$[OH]+NO_2 + M \rightarrow HNO_3 \quad (8)$$

$$[OH]+NO + M \rightarrow HONO + M \quad (9)$$

3. THE NOx REMOVAL MODEL

As can be seen, the above atmospheric reaction scheme can be conveniently used to treat NOx by artificial four staged treatment of exhaust streams containing NOx and CO as follows.

(i) Initiation of reactions (1), (2) and (3) where UV radiation acts on NO_2 and Ozone to produce singlet [O] atoms. The singlet [O] atoms react with moisture present to form [OH] radicals.
(ii) Induction of the second set of reactions (4) and (5) where the reactions of [OH] radicals with CO and O_3 to produce $[HO_2]$ radicals.
(iii) Subsequent induction of the third set of reactions presented in equations (6) and (7) where the $[HO_2]$ radicals react with NO and O_3 to produce further [OH] radical thus enhancing the second set of reactions followed again by the third set in a cyclic manner.
(iv) In the fourth sub set of reactions , NO_2 and NO undergo reactions with [OH] radicals to form HNO_2 and HNO_3.

The overall result of the reaction scheme is seen to produce CO_2 at the expense of [OH] radicals and HNO_2 and HNO_3 at the expense of $[HO_2]$ radicals. The reactions continue on a self sustaining basis once the reactions of the first set are triggered by UV and moisture to produce an [OH] radical. The reaction scheme of the proposed model is shown in Figure1.

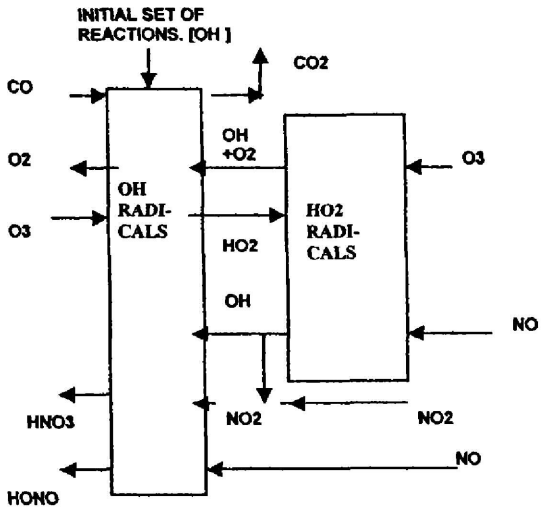


Figure 1. The Reaction Scheme

The rate constants for the second and third sets of reactions are available (Carpenter et al.,1998) for a temperature of 284K as follows.

TABLE 1 : Rate constants of reactions at 284 K

Symbol	Value ($/cm^3\ mol^{-1}\ s^{-1}$)
k_4	$2.4x10^{-13}$
k_5	$5.8x10^{-14}$
k_6	$8.9x10^{-12}$
k_7	$1.9x10^{-15}$
k_8	$1.3x10^{-}$
k_9	$5.4x10^{-12}$

3. DISCUSSION

The reaction (4) indicates that the role of CO in the production of $[HO_2]$ radicals. The $[HO_2]$ radicals in turn react with O_3 and NO in reactions (6) and (7) depleting NO as well as producing [OH] radicals. The [OH] radicals in turn promotes depletion of NO and NO_2 to produce HNO_2 and HNO_3 as shown in reactions (8) and (9) showing the influence of CO in the overall NOx depletion reactions.

Making use of the rate constant parameters presented in Table 1 in equation (17) it can be shown that the fractional depletion of NOx per unit fractional conversion of CO (θ) varies from 22.5 to 54.17 for values of β= 1 and β=0. The case of β=1 represents that all NOx consist of NO and β=0 represents the case where all NOx consist of NO_2. In practice $0<\beta<1$. The above values are applicable to a temperature of 284K for which the rate constants have been presented in the literature. With knowledge of the activation energies of the respective reactions , it could be possible to obtain the values of β for other temperatures too. However, the order of magnitude of β with the temperature cannot be expected to vary in the order of magnitudes from the above values showing a high degree of the NOx depletion with respect to the depletion of CO. A plot of θ vs γ_1 and γ_2 (where γ_1 and γ_2 are the values of $[\{k_9/k_4\}_T/\ \{k_9/k_4\}_{284}]$and $[\{k_8/k_4\}_T/\ \{k_8/k_4\}_{284}]$) is presented in Figure 2. Here $k_9/k_4\}_T$ and $k_8/k_4\}_T$ are the values of k_9/k_4 and k_8/k_4 at a temperature T°K. The upper and lower lines in the figure represents the boundaries of θ for limiting values of β of 0 and 1 respectively. The working region of the model is therefore the strip between the two lines where $0<\beta<1$. This shows that the q value mainly falls above 1.0 indicating a high rate of fractional depletion of NOx per unit fractional depletion of CO.

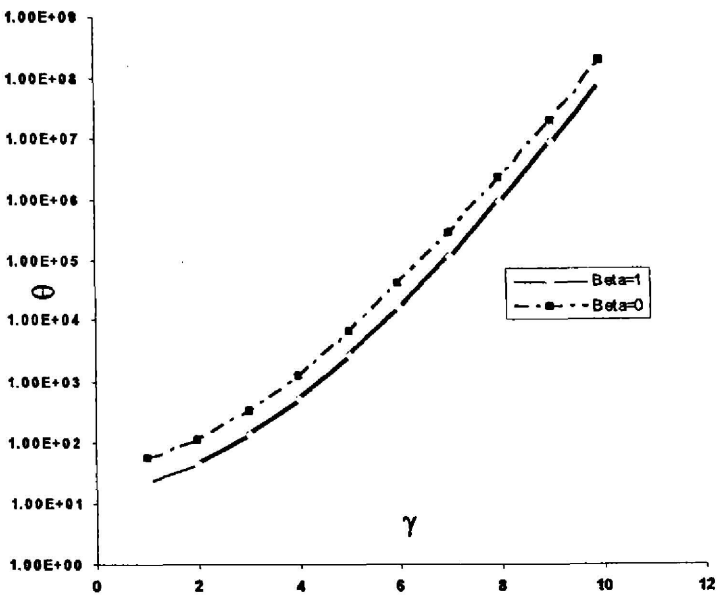
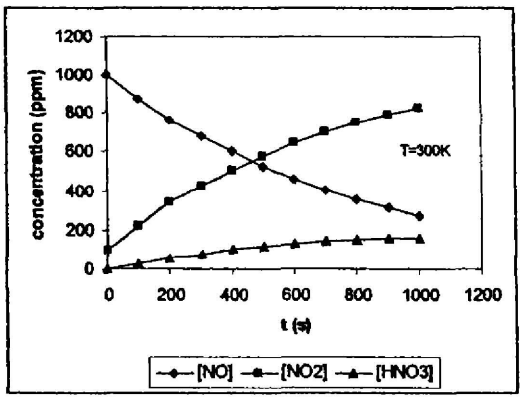


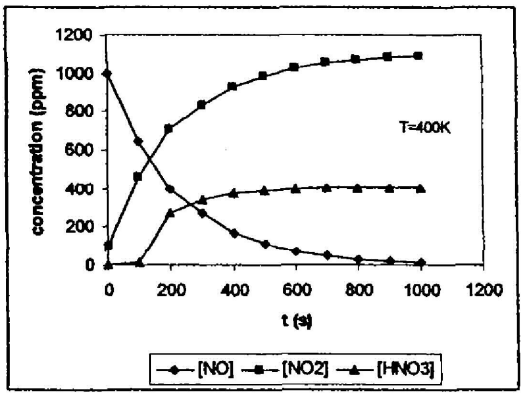
Figure 2: Plot of θ vs γ

$H+HO_2 \rightarrow 2OH$			√

3.2 Temperature Effect on NOx removal.

The effects of temperature on the NO_x removal was examined using simulated exhaust gas. The compositions of the exhaust gases were the same as those listed in Table 2. The time period studied for NO removal with ozone oxidation was approximately 1000s and the temperatures used for investigation were 300K, 400K and 500K. Fig. 4 shows the conversions in the different temperature within 1000s. At all temperature used for NOx removal show that NO was completely removed with the reaction at 500 K the fastest for NO removal. It was completely removed at 600s. Meanwhile the reaction at 400K was complete at 900K and the reaction at 300K was not complete even within 1000s. It showed that fast conversions at higher temperatures occur.





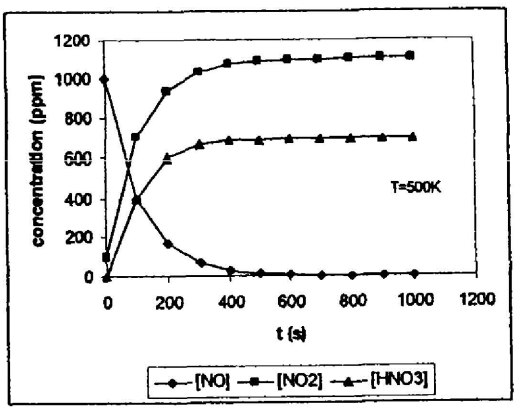


Fig.4: The comparison of conversions in the different temperature within 1000s.

4. CONCLUSION

A parametric investigation of time dependence NO and NO_2 oxidation using ozone is conducted by developing a reaction kinetic model using polymath with the input stream consisting of a simulated exhaust gas mixture. A chemical kinetic mechanism for low temperature reactions that occur involving the products of combustion and ozone is collated and employed in the calculations. It determined that the percentage of NO removal to form NO_2 is very good and time scale of oxidation of NO and NO_2 using ozone is low as several seconds. However the oxidation of the NO to NO_2 by ozonation process takes longer time when the O_3 and OH concentration used was low. The trend of NO consumption and NO_2 production were seen to be increasing with temperature.

5. REFERENCE

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